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(19)

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(54) IMPROVED HYDROFORMYLATION PROCESS

(71) We, UOP INC (formerly Universal Oil Products Company), a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, 60016, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for the production of an aldehyde and/or an alcohol.

Processes directed to the production of reaction mixtures comprising substantial amounts of aldehydes and alcohols by the hydroformylation of unsaturated compounds with carbon monoxide and hydrogen in the presence of certain catalysts are well-known in the art. The aldehydes and alcohols produced generally correspond to the compounds obtained by the addition of a carbonyl or carbinol group to an olefinically unsaturated carbon atom in the starting material with simultaneous saturation of the olefin bond. The process is known as hydroformylation and involves a reaction which may be shown by the general generic formula:

$$R_1-\underset{R_3}{\overset{R_2}{C}}=C-R_4+CO+H_2\xrightarrow[\Delta]{\text{catalyst}}R_1-\underset{H}{\overset{R_2}{C}}-\underset{R_4}{\overset{R_3}{C}}-\overset{H}{C}=O \text{ and/or } R_1-\underset{H}{\overset{R_2}{C}}-\underset{R_4}{\overset{R_3}{C}}-\underset{H}{\overset{OH}{C}}-H$$

where R_1, R_2, R_3, R_4 may be chosen from a group comprising an organic, halide or hydrogen radical.

It has been shown in the prior art that dicobalt octacarbonyl has generally been used as a catalyst for the hydroformylation of unsaturated compounds. This catalyst, which can be prepared from many forms of cobalt, usually decomposes rapidly unless high pressures of about 200—4500 pounds per square inch gauge of carbon monoxide are maintained. Correspondingly, high pressures of hydrogen are also necessary. Another serious disadvantage of hydroformylation processes has been the necessity of proceeding in two steps when alcohols are desired products. Another disadvantage inherent in the hydroformylation is a relative inability to direct the reactions involved to the production of predominantly terminal alcohols when olefins contain more than 2 carbon atoms, particularly when the charge to the process comprises primarily internal olefins. Still another and more basic problem in a hydroformylation reaction is the production of alkanes which comprise an almost worthless by-product of the hydroformylation reaction.

In contradistinction to the prior art, it has now been shown that the presence of carbon dioxide in the hydroformylation of an unsaturated compound by carbon monoxide and hydrogen in the presence of a catalyst comprising a cobalt-containing compound, the carbon dioxide being present in an amount of at least 0.5 moles (preferably at least 0.8 moles) per mole of carbon monoxide) will greatly decrease

the quantity of contaminating alkanes produced by the hydroformylation reaction. As will be appreciated from the specific Examples which follow the present invention enables the skilled man, in manufacture of the alcohols and aldehydes, to maintain a better percentage conversion of the original unsaturated compound while also reducing need for the treatment of undesirable products as a result of the lower quantity of alkanes formed in the hydroformylation. The utilization of the present invention will also allow the manufacturer to reduce his costs of production and thereby eventually reduce the cost of the alcohols and the aldehydes to the consumer.

The desired products to the process of this invention, namely alcohols and aldehydes, are utilized in the chemical industry in many ways. For example, alcohols are utilized in the synthesizing of other organic derivatives, as solvents, as an extraction medium, in dyes, synthetic drugs, synthetic rubber, detergents, cleaning solutions, surface coatings, cosmetics, pharmaceuticals, in the preparation of esters, as a solvent for resin in coatings, as a plasticiser, dyeing assistant, hydraulic fluids, detergent formulations, dehydrating agents, or the use of aldehydes as exemplified by their utility as perfumeries, or in the synthesis of primary alcohols.

According to the invention, there is provided a process for the production of an aldehyde and/or an alcohol which process comprises effecting hydroformylation of an unsaturated compound by reaction with carbon monoxide and hydrogen in the presence of a catalyst comprising a cobalt-containing compound and in the presence of carbon dioxide in an amount of at least 0.5 moles per mole of carbon monoxide.

The amount of carbon dioxide present will conveniently be on a molar basis, approximately equal to, or in excess of, the amount of carbon monoxide present. Preferably, the amount of carbon dioxide will be from 1 to 2.5 times the partial pressure of the carbon monoxide employed.

A specific embodiment of this invention resides in a process for preparing undecanal (undecylaldehyde) which comprises the treatment of decene-1 with carbon monoxide in the presence of dicobalt octacarbonyl and carbon dioxide at a temperature in the range of about 100°C. to about 200°C. and a pressure in the range of about atmospheric to about 5 atmospheres and recovering the resultant undecanal (undecylaldehyde).

Another specific embodiment of this invention resides in a process for preparing a mixture of dodecanol-1, 2-methylundecanol-1, 2-ethyldecanol-1 and 2-propylnonanol-1 which comprises the treatment of a mixture of undecane-5, dodecane-4, tridecane-6 and tetradecene-4 with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl, diethylphenyl phosphine and carbon dioxide at a temperature of 195°C. and a pressure of 100 atmospheres and recovering the resultant mixture of dodecanol-1, 2-methylundecanol-1, 2-ethyldecanol-1, 2-propylnonanol-1, tridecanol-1, 2-methyldodecanol-1, 2-ethylundecanol-1, tetradecanol-1, 2-methyltridecanol-1, 2-ethyldodecanol-1, pentadecanol-1, 2-methyltetradecanol-1, and 2-ethyltridecanol-1.

The hydroformylation reaction is in general effected under conditions which include a temperature in the range of from 75°C. to 300°C. and preferably in a range of from 100°C. to 200°C. The pressure employed will in general range from atmospheric up to 500 atmospheres or more. When superatmospheric pressures are employed, said pressure is usually afforded by the introduction of gaseous carbon monoxide, hydrogen and carbon dioxide to the reaction zone. Examples of suitable unsaturated compounds which are utilized as the starting material in the hydroformylation process of this invention include, in particular, propylene, butene-1, butene-2, isobutene, pentene-1, pentene-2, 2-methylbutene-1, 2-methylbutene-2, hexene-1, 3-methylpentene-1, 2-methylpentene-2, heptene-2, 2-methylhexene-2, 3-methylhexene-2, octene-1, octene-2, 3-methylheptene-1, 2-methylheptene-2, nonene-3, 3-methyloctene-2, decene-2, decene-5, 3,4-dimethyloctene-2, 4-ethyloctene-2, undecene-3, undecene-4, 4-methyldecene-2, 4,5-dimethylnonene-2, dodecene-3, tridecene-2, tetradecene-3, pentadecene-5, heptene-1, nonene-1, decene-1, decene-2, decene-3, decene-4, decene-5, undecene-1, undecene-2, undecene-3, undecene-4, undecene-5, didecene-1, dodecene-3, dodecene-5, tridecene-1, tridecene-3, tridecene-4, tridecene-6, tetradecene-1, tetradecene-2, tetradecene-7, pentadecene-1, pentadecene-4, pentadecene-6, 2-methoxybutene-2, 2-methoxypentene-1, 2-ethoxyhexene-1, 1-propoxyheptane-1, 2-methoxyoctene-1, 2,3-diethoxyundecene-3, 1-chlorobutene-2, 2-chloropentene-1, 2-bromohexene-2, 2,3-dichlorooctene-1, 3-iodooctene-2, 2-methoxy-3-chlorodecene-2, 3,4-dimethyl-2-chlorooctene-2, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclodecene, 1-methylcyclohexene-1, 1-ethylcyclohexene-1, 2,3-dipropylcycloheptene-1, 1-methoxycyclopentene-1, 1-chlorocycloheptene-

1, 2,3,4-trichlorocyclooctene-1, or mixtures of linear internal olefins such as internal olefins possessing carbon numbers of between 11 and 14 or 15 and 18.

It is understood that the aforementioned unsaturated compounds are only representative of the class of compounds which may be employed and that the present invention is not necessarily limited thereto.

The catalytic compositions of matter which are used in the process of this invention comprise compounds containing cobalt such as a tertiary organophosphine-cobalt carbonyl complex. The phosphorus-containing ligand component of the complex catalyst may thus suitably be a tertiary phosphine, such as trialkyl phosphine. The hydrocarbyl components need not necessarily be the same and suitable tertiary organophosphine ligands comprise the mixed phosphines wherein different members of the groups are comprised of alkyls, aryls, aralkyls and alkaryls. Preferred catalysts of the above-defined class comprise those wherein the hydrocarbyl component contains from about 1 to about 20 carbon atoms and the total number of carbons in the tertiary organophosphine group does not exceed about 30. A particularly preferred group of catalysts within the above-defined class are the trialkyl phosphine-cobalt carbonyl complexes wherein the phosphorus-containing component of the catalyst is a trialkylphosphine in which each alkyl is a lower alkyl having from 1 to about 10 carbons. Specific examples of suitable catalyst of the above-defined class comprise complexes between cobalt, carbon monoxide, and one of the following tertiary organophosphines: trimethylphosphine, triethylphosphine, tri-*n*-butylphosphine, triamylphosphine, trihexylphosphine, tripropylphosphine, trinonylphosphine, tridecylphosphine, di-*n*-butyl octadecylphosphine, dimethylethylphosphine, diamylethylphosphine, ethyl-bis-(β-phenylethyl)phosphine, tricyclopentylphosphine, tricyclohexylphosphine, dimethylcyclopentylphosphine, trioctylphosphine, diphenylmethylphosphine, diphenylbutylphosphine, diphenylbenzylphosphine, trilaurylphosphine, diethylphenylphosphine, etc.

It is also contemplated within the scope of the process of the present invention that the hydroformylation may be effected in an inert organic medium as exemplified by *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, isooctane (2,2,4-trimethylpentane), cyclohexane, methylcyclohexane, benzene and toluene.

It is understood that the aforementioned organophosphine-cobalt carbonyl complexes and inert organic media are only representative of the class of compounds which may be employed, and that the present invention is not necessarily limited thereto.

The process of this invention may be effected in any suitable manner and may comprise either a batch or continuous type operation. For example, when a batch-type operation is employed, the reactants comprising the unsaturated compound, carbon monoxide and hydrogen, may be placed in an appropriate apparatus along with a catalyst comprising a cobalt-containing compound, and carbon dioxide. The autoclave may then be sealed, heated to a desired operating temperature and maintained thereat for a predetermined residence time. At the end of this time, which may be from about 0.5 to 20 hrs. or more in duration, the heating can be discontinued, the autoclave allowed to return to room temperature and vented, thereby allowing the autoclave to return to ambient pressure, and the reaction mixture is then recovered, separated from the catalyst and subjected to conventional means of purification and separation, for example washing, drying, extraction, evaporation, fractional distillation, etc., whereby the desired alcohol or aldehyde is recovered.

It is also contemplated within the scope of this invention that the hydroformylation process for obtaining the desired alcohols and aldehydes may be effected in a continuous manner of operation. When such a type of operation is employed, the reactants comprising the unsaturated compounds may continuously be charged to the hydroformylation reaction zone containing the catalyst comprising a cobalt-containing compound, said hydroformylation zone being maintained at the proper operating conditions of temperature and pressure by heat and the admission of the requisite quantities of carbon monoxide, hydrogen and carbon dioxide, as required for effecting of the hydroformylation reaction. After completion of the desired residence time, the reactor effluent can continuously be withdrawn and subjected to conventional means of separation whereby the desired alcohols and/or aldehydes are recovered while carbon dioxide and any unreacted starting material comprising the unreacted unsaturated compound, carbon monoxide, or hydrogen, are recycled to the reaction zone to form a portion of the feed stock or a gaseous stream. The cobalt values may be recovered from the reaction mixture by various methods known to the art and regenerated to form fresh catalyst.

Examples of alcohols and aldehydes which may be prepared according to the

process of this invention will include butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, 2-methylbutanol-1, 2-methylpentanol-1, 2-ethylpentanol-1, 2-methylhexanol-1, 2-ethylhexanol-1, 2-chloropropanol-1, 3-chlorohexanol-1, 2,3-dichloroheptanol-1, 2-ethyl-3-chlorooctanol-1, butanal, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, 2-methylbutanal, 2-methyloctanal, cyclopentyl carbinol, cyclohexyl, carbinol, cycloheptyl carbinol, cyclooctyl carbinol, cyclononyl carbinol, cyclodecyl carbinol, cyclododecyl carbinol, mixed hydroxymethylalkanes, mixed formylalkanes, etc.

The following Examples are intended to illustrate the process of the present invention.

EXAMPLE I

In this Example, 143.0 millimoles of decene-5 was added to an 850 milliliter glass-lined rotating autoclave containing 1 millimole of dicobalt octacarbonyl and 4 millimoles of tri-*n*-butylphosphine in 5 milliliters of n-pentane, said rotating autoclave being equipped with heating and pressure attainment devices. The rotating autoclave was sealed, pressurized by the entry of 20 atmospheres of carbon monoxide and 80 atmospheres of hydrogen, heated to a temperature of 195°C., and maintained thereat for a period of time comprising 1 hour. At the end of the 1 hour period of time, the heating was terminated thereby allowing the rotating autoclave to return to room temperature and the carbon monoxide and hydrogen were carefully vented thereby allowing said autoclave to return to ambient pressure. At this point, the product was removed from the glass-lined rotating autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis disclosed the product to be a mixture of undecanol, 2-methyldecanol-1, and 2-ethylnonanol-1 plus minor quantities of the corresponding aldehydes with 71 percent of the oxygenated products comprising the linear constituents and a 32 percent conversion of the decene-5 to the decane. The approximate decene conversion was 100 percent.

EXAMPLE II

This experiment was performed to show the decrease of the undesirable alkane conversion from the unsaturated reactants during hydroformylation.

The experiment of Example I was reperformed with the maintenance of the physical variables at constant values with the exception of the addition of a new parameter, that being the addition of 20 atmospheres of carbon dioxide during the initial pressurizing of the rotating autoclave. After termination of the experiment, the product was again removed from the autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis disclosed the product to be a mixture of undecanol, 2-methyldecanol-1 and 2-ethylnonanol-1 plus minor quantities of the corresponding aldehydes was a 68 percent of the oxygenated products comprising the linear substituents and an 18 percent conversion of the decene-5 to the decane. The approximate decene conversion was 85 percent. It can be seen by the comparison of Examples I and II that the addition of carbon dioxide substantially reduced the quantity of the undesired decane produced.

EXAMPLE III

In this Example, 100.0 millimoles of condensed pentene-2 are placed in an 850 milliliter rotating autoclave containing .5 millimoles of a catalyst comprising a complex between cobalt, carbon monoxide and diethylphenylphosphine in 50 millimeters of n-heptane, said autoclave being equipped with a device for heating and pressure attainment. The rotating autoclave is heated to a temperature of 250°C., after being pressurized with 80 atmospheres of hydrogen, 20 atmospheres of carbon monoxide and 50 atmospheres of carbon dioxide and maintained thereat for a period of time comprising 1 hour. At the end of the 1 hour period of time, the heating is terminated, thereby allowing the rotating autoclave to return to room temperature, the rotating autoclave is vented, thereby allowing the rotating autoclave to return to ambient pressure. At this point, the product is removed from the rotating autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis discloses the product to be a mixture of hexanol-1, 2-methylpentanol-1 and 3-ethylbutanol-1 possessing a lesser amount of pentane than is normally obtained in a similar hydroformylation reaction when carbon dioxide had not been utilized.

EXAMPLE IV

In this Example, 93.0 millimoles of heptene-3 are placed in an 850 milliliter rotating autoclave containing 1.5 millimoles of a catalyst comprising a complex between

cobalt, carbon monoxide and dimethylcyclohexylphosphine in 20 milliliters of *n*-pentane, said autoclave being equipped with devices for heating as well as for maintaining a flow of carbon monoxide, carbon dioxide and hydrogen. The rotating autoclave it initially charged with 25 atmospheres of carbon dioxide, 10 atmospheres of carbon monoxide and 40 atmospheres of hydrogen, heated to a temperature of 200°C. and maintained thereat for a period of time comprising one hour. At the end of 1 hour period of time, the heating is terminated thereby allowing the rotating autoclave is return to room temperature, the flow of carbon monoxide, carbon dioxide and hydrogen is terminated and the rotating autoclave is vented thereby allowing said autoclave to return to ambient pressure. At this point, the product is removed from the rotating autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis discloses the product to be a mixture of octanol-1, 2-methylheptanol-1, and 2-ethylhexanol-1 possessing lesser amounts of heptane than is produced in a similar hydroformylation when carbon dioxide had not been utilized.

EXAMPLE V

In this Example, 95.0 millimoles of decene-1 are placed in an 850 milliliter rotating autoclave containing 2.0 millimoles of a catalyst comprising dicobalt octacarbonyl in 15 milliliters of *n*-heptane, said autoclave being equipped with heat and pressure devices. The rotating autoclave is pressurized by the addition of 20 atmospheres of carbon dioxide, 50 atmospheres of hydrogen and 25 atmospheres of carbon monoxide, heated to a temperature of 275°C. and maintained thereat for a period of time comprising 1 hour. At the end of the 1 hour period of time, the heating is terminated thereby allowing the rotating autoclave to return to room temperature, the flow of carbon dioxide, carbon monoxide and hydrogen is terminated and the rotating autoclave vented thereby allowing said autoclave to return to ambient pressure. The product is removed from the rotating autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis discloses the product to be predominantly undecanol-1 and 2-methyldecanol-1 possessing lesser amounts of decane than is formed in a similar hydroformylation reaction when carbon dioxide is not utilized.

EXAMPLE VI

In this Example, 91.3 millimoles of tetradecene-7 are placed in an 850 milliliter rotating autoclave containing 1.0 millimoles of a catalyst comprising a complex between cobalt, carbon monoxide and tri-decylphosphine in 100 milliliters of *n*-pentane, said autoclave being equipped with devices for heating as well as for a flow of carbon monoxide, carbon dioxide and hydrogen. The rotating autoclave is pressurized by the forced entry of 45 atmospheres of hydrogen, 25 atmospheres of carbon monoxide and 35 atmospheres of carbon dioxide, heated to a temperature of 175°C., and maintained thereat for a period of time comprising 1 hour while the maximum pressure developed during the reaction is maintained by the addition of gas from an independent reservoir containing a two to one molar mixture of hydrogen and carbon monoxide. At the end of the 1 hour, the heating is terminated thereby allowing the rotating autoclave to return to room temperature, the flow of carbon monoxide and hydrogen is terminated and the rotating autoclave vented thereby allowing said autoclave to return to ambient pressure. The product is removed from the rotating autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis discloses the product to be a mixture of pentadecanol-1, 2-methyltetradecanol-1 and 2-ethyltridecanol-1 and possessing similar amounts of tetradecene than would be formed in a similar hydroformylation reaction when carbon dioxide has not been utilized.

EXAMPLE VII

In this Example, 75.6 millimoles of a mixture comprising undecene-5, dodecene-4, tridecene-6 and tetradecene-4 are placed in an 850 milliliter rotating autoclave containing 1.1 millimoles of a catalyst comprising a complex between cobalt, carbon monoxide and trinonylphosphine in 90 milliliters of *n*-pentane, said autoclave being equipped with devices for heating as well as for a flow of carbon monoxide, carbon dioxide and hydrogen. The rotating autoclave is pressurized by the force entry of 40 atmospheres of hydrogen, 25 atmospheres of carbon monoxide and 30 atmospheres of carbon dioxide while the maximum pressure developed during the reaction is maintained by the addition of gas from an independent reservoir containing a two to one molar mixture of hydrogen to carbon monoxide, heated to a temperature of 225°C. and maintained thereat for a period of time comprising 45 minutes. At the

end of the 45 minute period of time, the heating is terminated thereby allowing the rotating autoclave to return to room temperature, the flow of carbon monoxide and hydrogen is terminated and the rotating autoclave vented thereby allowing said autoclave to return to ambient pressure. The product is removed from the rotating autoclave and analyzed by means of gas-liquid chromatography instrumentation, said analysis discloses the product to be a mixture of dodecanol-1, 2-methylundecanol-1, 2-ethyldecanol-1, 2-propylnonanol-1, tridecanol-1, 2-methyldodecanol-1, 2-ethylundecanol-1, tetradecanol-1, 2-methyltridecanol-1, 2-ethyldodecanol-1, pentadecanol-1, 2-methyltetradecanol-1, and 2-ethyltridecanol-1 possessing lesser amounts of undecane, dodecane, tridecane and tetradecane than would be formed in a similar hydroformylation reaction when carbon dioxide has not been utilized.

WHAT WE CLAIM IS:—

1. A process for the production of an aldehyde and/or an alcohol which process comprises effecting hydroformylation of an unsaturated compound by reaction with carbon monoxide and hydrogen in the presence of a catalyst comprising a cobalt-containing compound and in the presence of carbon dioxide in an amount of at least 0.5 moles per mole of carbon monoxide.

2. A process as claimed in claim 1 wherein the amount of carbon dioxide is at least 0.8 moles per mole of carbon monoxide.

3. A process as claimed in claim 1 or claim 2 wherein the carbon monoxide used constitutes a minor amount of the total volume of hydrogen, carbon monoxide and carbon dioxide.

4. A process as claimed in any one of claims 1 to 3 wherein the reaction is carried out at a temperature in the range of from 75°C to 300°C and under a pressure of from 1 atmosphere to 500 atmospheres.

5. A process as claimed in any preceding claim wherein the unsaturated compound is tetradecene-7 and the resultant hydroformylated compound is a mixture of pentadecanol-1, 2-methyltetradecanol-1 and 2-ethyltridecanol-1.

6. A process as claimed in any one of claims 1 to 4 wherein the unsaturated compound is pentene-2 and the resultant hydroformylated compound is a mixture of hexanol-1, 2-methylpentanol-1 and 3-ethylbutanol-1.

7. A process as claimed in any one of claims 1 to 4 wherein the unsaturated compound is heptene-3 and the resultant hydroformylated compound is a mixture of octanol-1, 2-methylheptanol-1, 2-ethylhexanol-1.

8. A process as claimed in any one of Claims 1 to 4 wherein the unsaturated compound is decene-1 and the resultant hydroformylated compound is a mixture of undecanol-1 and 2-methyldecanol-1.

9. A process as claimed in any one of Claims 1 to 4 wherein the unsaturated compound is decene-5 and the resultant hydroformylated compound is a mixture of undecanol, 2-methyldecanol-1, and 2-ethylnonanol-1.

10. A process as claimed in any one of Claims 1 to 4 wherein the unsaturated compound is a mixture of internal olefins and the resultant product is a mixture of primary alcohols.

11. A process as claimed in Claim 10 wherein the mixture of internal olefins comprises undecene-5, dodecene-4, tridecene-6 and tetradecene-4 and the resultant mixture of primary alcohols comprises dodecanol-1, 2-methylundecanol-1, 2-ethyldecanol-1, 2-propylnonanol-1, tridecanol-1, 2-methyldodecanol-1, 2-ethylundecanol-1, tetradecanol-1, 2-methyltridecanol-1, 2-ethyldodecanol-1, pentadecanol-1, 2-methyltetradecanol-1, and 2-ethyltridecanol-1.

12. A process as claimed in any preceding claim wherein the catalyst is a tertiary organophosphine-cobalt carbonyl complex.

13. A process as claimed in any preceding claim wherein the amount of carbon dioxide present is, on a molar basis, approximately equal to, or in excess of, the amount of carbon monoxide present.

14. A process as claimed in claim 13 wherein the partial pressure of the carbon dioxide employed is from 1 to 2.5 times the partial pressure of the carbon monoxide employed.

15. A process as claimed in any preceding claim wherein formation of aldehyde and/or alcohol takes place in a single reaction stage only.

16. A process for the production of an aldehyde and/or an alcohol, substantially as hereinbefore described with reference to any one of the foregoing Examples II to VII.

17. An alcohol and/or aldehyde when obtained by a process as claimed in any preceding claim.

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